Optimization and production of biodiesel from microalgae oil as jet fuel

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Abstract
Biodiesel is a type of liquid biofuel produced from renewable sources such as oils and fats and can be used as a replacement for fossil diesel in diesel engines. It emits far less pollutants than standard diesel fuel. In this study, the effect of two parameters of catalyst concentration and reaction time on the conversion rate of microalgae oil transesterification reaction at three levels was investigated by response surface methodology. The results of three-dimensional graph analysis using Minitab software showed that the highest biodiesel production from microalgae oil was obtained at 1.2% (w/w) catalyst concentration and 60 min reaction time. Under these conditions, the conversion rate of microalgae oil to biodiesel was 77.85% and also according to GC-MS analysis the reaction conversion to methyl ester was over 90%. Comparison of the biodiesel combustion heat obtained (40.2 j/g) with other jet fuels indicates that the resulting biodiesel performance is very close to the JP-4 fuel.

Keywords: Biodiesel, Production, Optimization, Response surface, GC-MS, Microalgae, Biofuel, Design expert, Transesterification, Jet fuel, Biojet

Introduction
Half of renewable energy consumption in 2017 was devoted to bioenergy. A 30% increase in biofuel consumption in 2018 to 2023 will make it the largest source of energy. According to ICAO[1] and IATA[2], with the replacement of biofuels such as biojet and its use, we will see a 1.5% annual reduction in CO_2 emissions and a 50-95% reduction by 2050[1]. In 2010, CO_2 emissions were 448 (Mt) from aerial fuels, and it is projected to increase by 2020 to 682-775 (Mt) and by 2050 to more than 2700 (Mt) Found. Fuel consumption in the aviation industry is projected to reach 852(Mt) by 2050, requiring 426(Mt) jet biofuel to reduce emissions by 50%, while recent biojet production is very limited and less than 0.1% The global total consumption of different types of jet fuel reaches. Due to the similarity of the molecular structure of biodiesel oil with that of crude oil and Petroleum Products, the jet engine does not need to be changed or modified when using these fuels. Adding 1 to 2 percent biodiesel to the diesel fuel mix has an additive effect on lubrication to maintain the anti-corrosion properties of the spray system[2,3,4]. Among the different methods of converting oil to biodiesel, the

[1] International Civil Aviation Organization
[2] International Air Transport Association

best method for overcoming the problem of high viscosity is esterification method. There are generally three methods of producing methyl ester by transesterification, including base transesterification, acid transesterification, lipase enzymatic transesterification[5]. Benefits of micro-algal biojet include reducing fuel consumption by 5-10% compared to oil-based fuels, cleaner production by consuming 10 times more CO_2 than other bio-sources, non-competitiveness with the food industry, also it has made the soil fertile and reducing water salinity[6]. In this study, due to the higher amount of free fatty acids in microalgae oil than its maximum permitted (0.5% w / w), two step transesterification method is used for biodiesel production. Also, two of the most effective factors in the esterification process, including catalyst concentration and reaction time, are optimized by designing experiments using response surface methodology over 13 experiments.

Experimental

One of the most important factors affecting the success of the biodiesel production reaction is the quality of the process oil. Several studies have suggested that the amount of free fatty acids (FFA) in the oil should be less than 0.5 wt% of the oil used. For this reason at first measure the amount of these free fatty acids in the oil (equation1) For this purpose titration of existing oils was carried out using 0.1N potassium hydroxide solution and phenolphthaline reagent.

$$\%FFA = \frac{0.5 \times A \times N \times Wc}{W} = \frac{0.5 \times 0.75 \times 0.1 \times 56.1}{1} = 2.1\% \quad (1)$$

A: Volume of the base solution(mL), N:Normality, $W_{c:}$ Molecular mass of the catalyst(g), W: Oil weight(g)

The amount of free fatty acids for microalgae oil was 2.1%, which should be less than 0.5% by the esterification reaction. Considering the amount obtained, at first 1% (wt.%) of sulfuric acid (98% purity) is used as a catalyst and methanol with a molar ratio of 1 to 6 at 60°C with a rotation speed of 600 rpm acid esterification process within 1 hour is done to convert the free fatty acids into methyl ester and Secondly, using methanol with the same molar ratio, 1.2% (wt.%) of potassium hydroxide is used as the catalyst under the same conditions the base transesterification process is performed and triglycerides in microalgae oil are converted to biodiesel in a reversible process. After the transesterification process, the resulting solution is poured into the decanter to precipitate glycerol. After the glycerol separation, the solution is purified by warm water over several steps and poured into the decanter to remove the soap created due to the presence of the base catalyst. Continue washing until clear water settles in the decantor. In the final step, place the solution in a rotary evaporator to evaporate the residual methanol from solution and recover[7,8,9].

In this study, the experimental design of response surface methodology was used to optimize the effective reaction conditions and parameters and to obtain the best operating status. The purpose of using this method is to identify and analyze the variables affecting outputs with the least number of trials. Many factors such as the type and amount of catalyst, the type and amount of acid, the type of alcohol and the ratio of alcohol to oil, temperature, pressure, stirring rate and method of testing in biofuel production are discussed but some are more effective and are operational factors. The parameters investigated in optimization of this study are the catalyst concentration and reaction time which are the most important operating parameters according to the information available in the sources. Table 1 shows the levels of each factor based on the initial experiments and the values in the sources and table 2 shows the order of the experiments and the conditions for each experiment. The experiments designed in this study were performed by Minitab software. The most common method for analyzing biodiesel samples and obtaining yield rates and conversion rates is the use of GC-MS chromatography. In this study, we also measured the biodiesel combustion heat produced by a bomb calorimeter to compare the biodiesel produced with jet fuel and investigate the possibility of replacing it with fossil fuels[3].

Table 1: Factors and levels examined in this study to achieve the optimal point

Factors \ Levels	Equation variables	-1	0	1
Catalyst (wt%)	X_1	1.1 %	1.2 %	1.3 %
Time (min)	X_2	50	60	70

Table 2: Arrangement of Experiments and Conditions of each Experiment to determine the optimal conditions with conversion rates

Test order \ Factors	Catalyst (wt%)	Time (min)	conversion rates (%)
1	1.3%	70	55.9 %
2	1.2%	60	49.9 %
3	1.1%	70	48.16 %
4	1.2%	60	77.85 %
5	1.3%	50	58.65 %
6	1.1%	50	51.15 %
7	1.2%	60	60 %
8	1.2%	39	51.55 %
9	0.85%	60	52.13%
10	1.2%	77.21	53%
11	1.2%	60	64.3 %
12	1.2%	60	70.75 %
13	1.43%	60	60.85 %

Results and discussion

Analysis of variance is performed using Minitab software for the main response of the reaction conversion percentage. The equation obtained by the software (Equation 2), indicate that the optimization process in this study is a first-order model and both parameters have a positive effect on the methyl ester efficiency and conversion rate. The catalyst concentration parameter has a greater influence on the process than the reaction time.

$$Yield = 30.3 + 2.58\ X_1 + 0.79\ X_2 \quad (2)$$

According to Fig 1, which illustrates the influence of variables on output efficiency in 3D graphs, darker spots have a higher yield that can be considered as optimal points. It can be seen from the graphs that there are higher-yielding points or darker points in the center of the shapes that consequently, appropriate ranges for the parameters are considered and acceptable experiments are designed to determine the optimal point. Also by examining Table 2, experiments with 1.2% catalyst concentration within 60 minutes have higher yields than other experiments which shows that the designed experiments have obtained good optimum points that it has been able to produce more than 70% in low time with proper catalyst concentration.

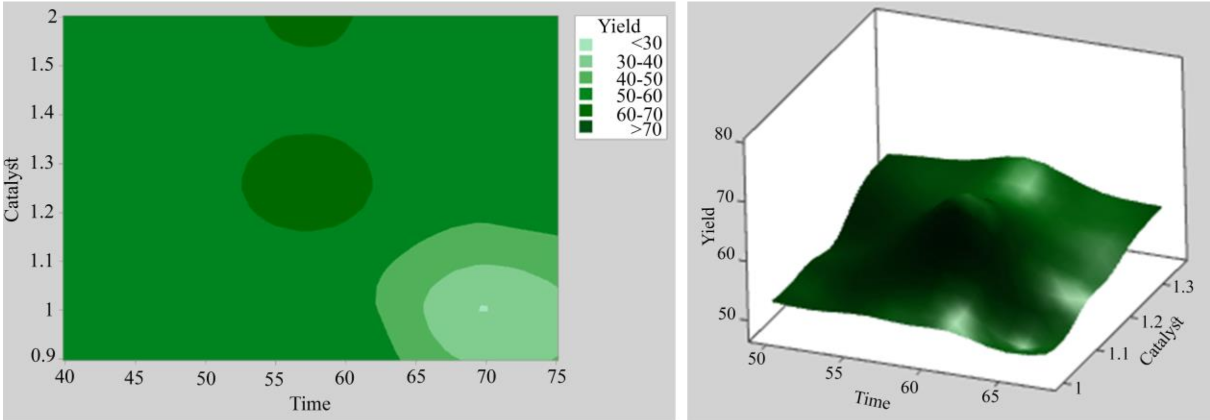

Figure1: Effect of parameters investigated on methyl ester production process and efficiency

Combustion heat is the amount of heat that the fuel releases and burns under ambient conditions. The combustion heat range of diesel fuel is 40-45 (Mj/Kg) while the combustion heat measured by the calorimeter bomb for the biodiesel produced in this study shows 40.2 (Mj/Kg) by comparing these two values, it can be concluded that the produced biodiesel can be replaced by diesel fuel without modifying the engine. Also, by comparing the biodiesel combustion heat produced with the fuel used in the aviation industry, the value obtained is very close to the JP-4 fuel combustion heat as a result, it can also be used on jet engines and aircraft without modification.

Gas chromatography has played a key role in the separation and quantification of a mixture but the determination of the nature and chemical structure of the separated components requires spectroscopic detection methods the most commonly used method is a mass spectrometer detector which allows to obtain a mass spectrum for a molecule that resembles its fingerprint. A chromatogram is a graph in which the detector responses to the sample components by leaving parts of the column (retention time) are plotted. According to Figure 2, the first output material Methyl myristate in 31 minutes and the peaks of Methyl palmitate and 11-Octadecenoic acid, methyl ester and Methyl stearate were got out of from column according to their retention time of 36.136, 39.657 and 39.914, respectively and they also have the highest area in the chart due to the their area below the peak, which has achieved excellent quality of 99%. As can be seen all the fatty acids have been converted to methyl ester with very high efficiency. In the area under the curve method, by dividing the area under the curve of each component by the total surface area of the component, the percentage surface area of each component is approximately the weight percent of that component. Each chromatogram consists of several peaks as shown in Figure 2 and Table 3, each peak belongs to a sample component. Mass spectrometry is an analytical method from which quantitative and qualitative information can be obtained on the molecular weight and molecular structure of organic and inorganic compounds whereby produced biodiesel starts from the 15-carbon fatty acids chain and continues to 25-carbon fatty acids and also the quality of the sample components indicates that the transesterification reaction yield as well as its conversion rate was very good and acceptable. This method can be used for qualitative analysis and identification and determination of different organic matter.

Table 3 Fatty Acid Compounds in Microalgae Biodiesel with Retention Time and area

No	RT (min)	Area (Ab*s)	Area%	Name	Quality
1	31.853	31781929	0.3	Methyl myristate	98
2	35.59	20384483	0.2	9-Hexadecenoic acid, methyl ester, (Z)-	99
3	36.136	1301547967	14.1	Methyl palmitate	99
4	37.495	9641727	0.1	Cyclopropaneoctanoic acid, 2-hexyl-, methyl ester	83
5	37.948	9447521	0.1	Heptadecanoic acid, methyl ester	98
6	39.657	7100486351	76.7	11-Octadecenoic acid, methyl ester	99
7	39.914	346049208	3.7	Methyl stearate	99
8	40.913	12880101	0.1	Methyl linoleate	93
9	42.57	8165498	0.1	1-(4'-pentenyl)-1,2-epoxycyclopentane	89
10	42.838	129711893	1.4	11-Eicosenoic acid, methyl ester	99
11	43.26	85746195	0.9	Eicosanoic acid, methyl ester	99
12	46.081	43506289	0.5	13-Docosenoic acid, methyl ester, (Z)-	93
13	46.462	56901716	0.6	Docosanoic acid, methyl ester	99
14	49.097	13951570	0.2	15-Tetracosenoic acid, methyl ester	99
15	49.437	29590537	0.3	Methyl lignocerate	99

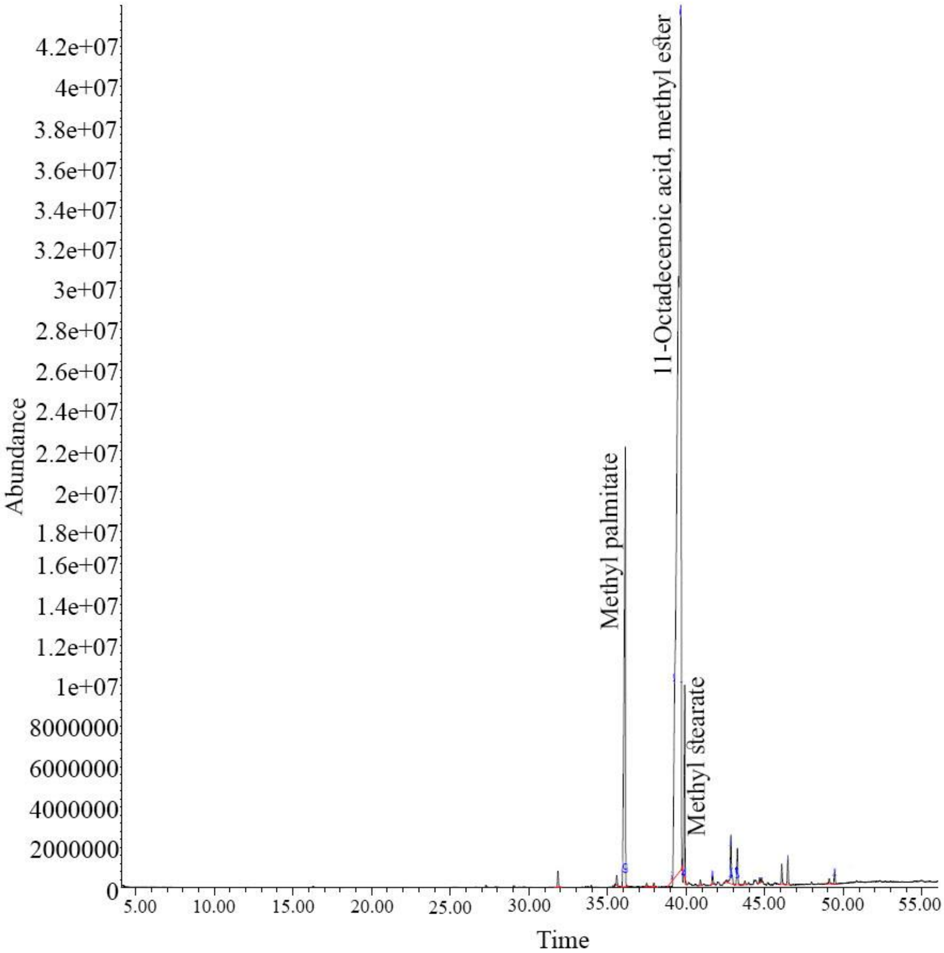

Figure 2: GC-MS Results, Fatty Acid Compounds in Microalgae Biodiesel

Conclusions

According to studies, two parameters of catalyst concentration and reaction time were optimized as the most effective factors in 13 experiments. According to the results obtained from the response surface methodology, the best operating conditions for maximum methyl ester production were achieved with extraction rate of 77.85% in molar ratio of methanol to oil, 6 to 1 and with catalyst concentration of 1.2% at 60 ° C during 1 hour. According to GC-MS analysis, the biodiesel produced under the optimum conditions has ۹۹% methyl ester that indicating high process efficiency. Due to the reduced viscosity of biodiesel compared to standard diesel and high methyl ester percentage in biodiesel, it can also be concluded that by comparing the calorimeter bomb results, comparing the biodiesel combustion heat with standard diesel, biodiesel can be a good alternative to diesel engines and jet engines that have the same performance as diesel without the need to change the engine.

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